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# Electronic Structure of an Iron-Porphyrin−Nitrene Complex

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Middle and late transition metal imido complexes (which may also be viewed as metal−nitrene adducts) are rather rare, especially for square-pyramidal and octahedral coordination geometries. However, an iron(II) porphyrin aminonitrene adduct, denoted here as Fe(Por)(NN), has been known for almost a quarter of a century. Unlike the corresponding $S = 1$ oxene and $S = 0$ carbene adducts, Fe(Por)(NN) exhibits an $S = 2$ ground state. DFT calculations reported herein provide a molecular orbital description of this unusual species as well as a rationale for its $S = 2$ ground state. The electronic configuration of Fe(Por)(NN) may be described as $d_{\pi}{}^2 d_{xy}{}^1 d_{z^2}{}^1 d_{x^2-y^2}{}^1 d_{\pi'}{}^1$, where the $z$ direction corresponds to the Fe−NN axis. The stability and double occupancy of one of the $d_{\pi}$ orbitals may be attributed to a $\pi$-backbonding interaction with the N−N $\pi^*$ orbital. The weak $\sigma$-donor ability of the aminonitrene ligand results in a relatively low-energy $d_{z^2}$ orbital and an overall d orbital splitting pattern that engenders a high-spin ground state.

## Introduction

Compared with the plethora of oxo and imido complexes involving early transition metals,[1,2] relatively few such complexes are known for middle and late transition metals. This should not be altogether surprising in view of the prohibitive $d_{\pi}-p_{\pi}$ antibonding interactions associated with relatively high d electron counts. One productive avenue for synthesizing middle and late transition metal imido/nitrene complexes has involved the use of low-coordinate architectures that by and large avoid occupancy of the high-energy $d_{\pi}-p_{\pi}$ antibonding orbitals. Thus, recent years have seen a dozen or so reports of trigonal-planar,[3,4] pseudotetrahedral,[5,6] and square-planar[7,8] imido complexes of middle and late first-row transition metals.[9,10]

Against this context, iron-imido/nitrene porphyrins are largely unknown,[11] although iron(IV)-oxo species are well-known as reactive intermediates of heme proteins and their synthetic models.[12] Twenty-five years ago, however, Mansuy and co-workers reported stable iron-porphyrin−nitrene adducts,[13,14] which to this day remain the only well-characterized examples of such species. Recently, Que and co-workers have reported another example of a *non-low-coordinate* iron-imido complex, although being a much more reactive species, it has only been spectroscopically characterized so far.[15]

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The electronic structures of these rare non-low-coordinate[16] iron-imido complexes, which are clearly of great interest, have not been the subject of detailed theoretical studies, a gap in our knowledge that we[6a] and others[17] have sought to redress. Very recently, Shaik[17] and co-workers presented an in-depth DFT study of nitrene transfer[18] mediated by iron porphyrins. The unique heme-nitrene adducts synthesized by Mansuy and co-workers, however, have never been the subject of a theoretical study since they were reported in 1984. Here, we present such a study.

The iron-nitrene porphyrins synthesized by Mansuy and co-workers, including one that was structurally characterized, are rather special. We symbolize them as Fe(Por)(NN), where Por denotes a porphyrin ligand and NN is a dialkylhydrazido or dialkylaminonitrene ligand. The stability of these complexes may be contrasted with the high reactivity[16,19,20] of analogous complexes with simple nitrene (i.e., alkyl- or arylnitrene) ligands. Another interesting feature of the NN complexes is their $S = 2$ ground state, which is apparently at odds with the $S = 0$ ground states of analogous heme-carbene[21,22] adducts and the $S = 1$ ground states of heme-oxene (i.e., $Fe^{IV}O$) species. The issue of spin states is also of interest from a methodological point of view, as DFT often struggles to give a good description of the spin state energetics of transition metal complexes,[23,24] the problem being particularly acute for iron complexes.[25]

## Methods

In general, all calculations were carried out with the OLYP[26,27] generalized gradient approximation (GGA), Slater-type triple-$\zeta$ plus polarization (TZP) basis sets, a fine mesh for numerical integration of matrix elements, and full geometry optimizations, all as implemented in the ADF 2007[28] program system. As a check on the performance of the OLYP energetics, we also employed the older PW91[29] GGA and the hybrid functionals B3LYP[30] and B3LYP*[31] for selected calculations.

## Results

**A. Structural Chemistry.** Figure 1 depicts highlights of the OLYP/TZP optimized geometries of the lowest-energy $S = 0$, 1, and 2 states of the Fe(P)(NN) model complex. From here onward, for simplicity, we will use P and NN to refer to unsubstituted porphyrin and 2,2,6,6-tetramethyl-1-piperidylnitrene, respectively. For each spin state, we examined different conformations of the piperidine ring. However, for all three spin states, the chair, boat, and twist conformations had very similar energies. Properties specific to each conformation are shown in Table S1 in the Supporting Information. The results shown in Figure 1 are for the twist conformation. Throughout, we have used unsubstituted porphyrin to model the *meso*-tetraarylporphyrins used in the experimental study,[13] a justifiable simplification, considering that we are primarily interested in examining the effect of the axial nitrene ligand.

The optimized geometry parameters do not merit much comment except that, for $S = 2$, the calculated and experimental[13] geometry parameters are generally in very good agreement (see Table S1 for details, Supporting Information). That said, the $Fe-N_{axial}$ and $N-N$ distances vary remarkably little among the three spin states shown in Figure 1. For all three spin states, the $Fe-N_{axial}$ distance is rather short, $< 1.9$ Å, which suggests at least partial multiple bond character.

For the $S = 2$ optimized geometry, the iron atom is displaced by nearly 0.6 Å, relative to the mean plane of the four porphyrin nitrogens. Such a strong displacement is typical of high-spin, five-coordinate iron porphyrins and reflects (half-)occupancy of the in-plane iron $d_\sigma$ orbital (i.e., the $d_{x^2-y^2}$ orbital). The calculated displacement is in fair but not excellent agreement with the experimentally observed displacement of 0.49 Å.[13] However, the fact that the crystal structure analysis was for a substituted porphyrin may account for part of the discrepancy. From the molecular orbital (MO) description given below, we will see that this geometrical feature is indeed as expected.

**B. Spin State Energetics.** As shown in Table 1, the relative energies of the three spin states vary somewhat among the four functionals that we have used in this study. Thus, although PW91 predicts an $S = 1$ ground state by a clear margin of energy, OLYP, B3LYP*, and B3LYP all predict an $S = 2$ ground state, as demanded by the experimental results. Moreover, the energetics obtained with the latter three functionals, which are in good mutual agreement, clearly indicate the following energy ordering: $S = 2 < S = 1 < S = 0$.

The behavior of the functionals observed here is fairly typical of what we and others have observed elsewhere.[22-24] Classic pure functionals such as PW91 and BP86 tend to unduly pair up electrons, whereas B3LYP generally behaves oppositely. The newer pure functional OLYP (or OPBE,[25d] which behaves nearly identically)

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[16] We use the somewhat cumbersome term non-low-coordinate to refer to coordination numbers higher than 4. In effect, the term refers to square-pyramidal and octahedral geometries.

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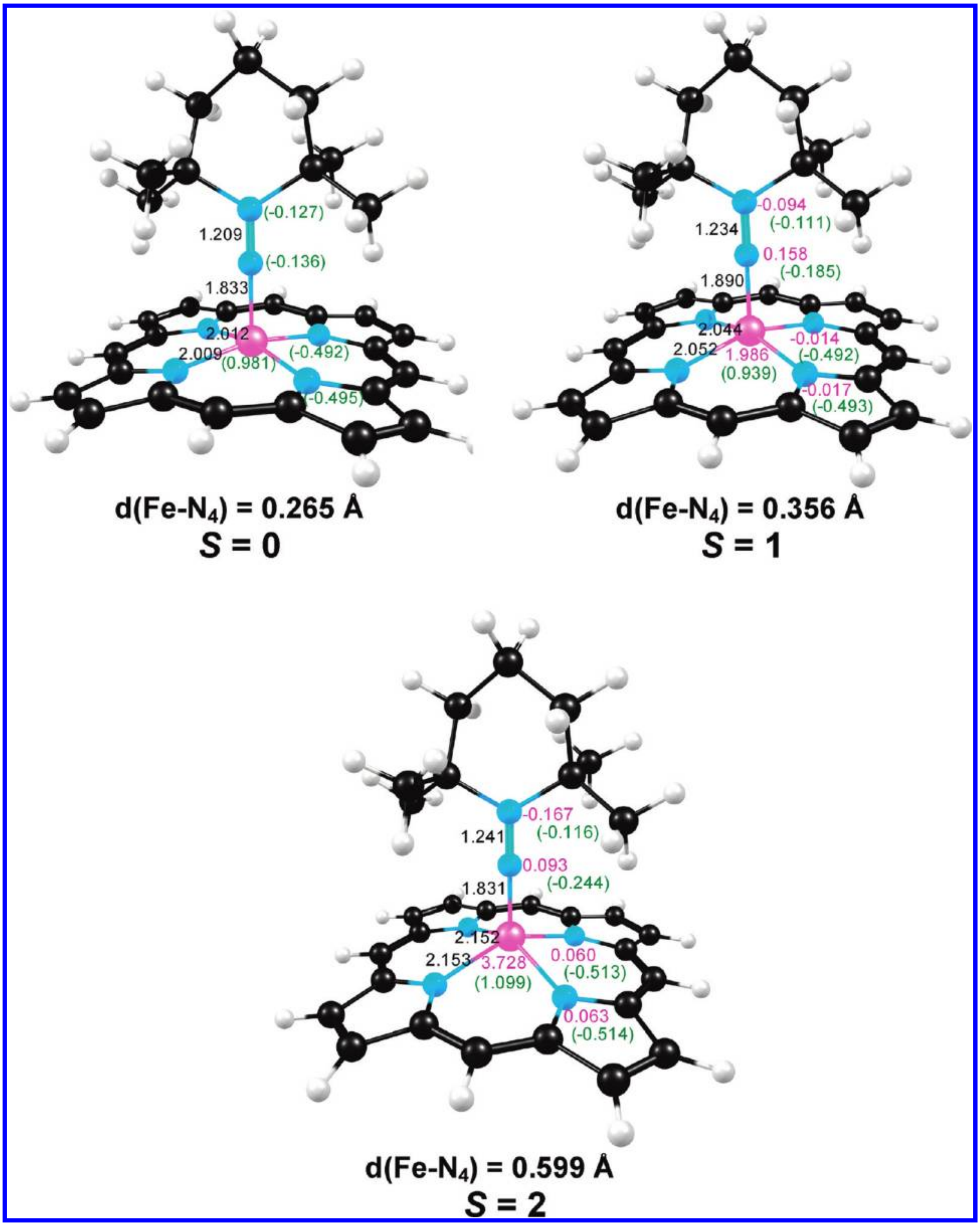

**Figure 1.** Highlights of OLYP/TZP optimized distances (Å, in black), Mulliken charges (green), and spin populations (magenta) for the $S = 0$, 1, and 2 states of Fe(P)(NN). A twist conformation has been assumed for the piperidine ring, resulting in an overall $C_2$ point group.

and the hybrid functional B3LYP*, which has a reduced amount of Hartree−Fock exchange (15%) relative to B3LYP (20%), are sometimes a good compromise. In certain other cases, however, B3LYP has provided the best energetics for the range of functionals examined.[25c] The fact that OLYP, B3LYP*, and B3LYP all predict very similar energetics is reassuring and suggests that they provide a faithful representation of reality.

**C. Molecular Orbital Description.** We are now in a position to address the key chemical questions: What accounts for the $S = 2$ ground state and "where" are the electrons? Figure 2a,b present the OLYP MO energy level diagrams for the $S = 0$ and $S = 1$ states, respectively. The

**Table 1.** Energetics of Different Spin States and Conformations of Fe(P)(NN)[a]

| | | relative energy (eV) | | | |
|---|---|---|---|---|---|
| piperidine conformation | $S$ | OLYP | PW91 | B3LYP | B3LYP* |
| boat | 0 | 0.99 | 0.26 | 0.97 | 0.79 |
| | 1 | 0.31 | −0.22 | 0.33 | 0.19 |
| | 2 | −0.01 | −0.04 | 0.00 | −0.01 |
| chair | 0 | 0.94 | 0.19 | 0.94 | 0.76 |
| | 1 | 0.25 | −0.34 | 0.27 | 0.13 |
| | 2 | −0.07 | −0.08 | −0.06 | −0.06 |
| twist | 0 | 0.99 | 0.24 | 0.98 | 0.80 |
| | 1 | 0.31 | −0.25 | 0.34 | 0.20 |
| | 2 | **0.00** | **0.00** | **0.00** | **0.00** |

[a] The $S = 2$ state for the twist conformation has been chosen as the zero level for energies.

electronic configuration of the $S = 0$ state may be described as $d_\pi{}^2 d_{xy}{}^2 d_{\pi'}{}^2$, as expected from elementary ligand field theory considerations. Here, $d_\pi$ refers to the lowest-energy d orbital, which engages in a $\pi$-backbonding interaction with the N−N $\pi$* orbital. The other $d_\pi$ orbital, which we refer to as $d_{\pi'}$, is involved in a $\pi$-antibonding interaction with a lone pair on the nitrene ligand and, therefore, has a higher orbital energy. Interestingly, the LUMO of the $S = 0$ state, which is largely made up of the Fe $d_{z^2}$ orbital, is only slightly higher in energy. Not surprisingly, therefore, the $S = 1$ state is one of the low-energy states and, indeed, as mentioned above, the $S = 1$ state is lower in energy than the $S = 0$ state. Consistent with this analysis, Figure 2b shows that the Fe $d_{\pi'}$ and $d_{z^2}$-based MOs are nearly degenerate for the $S = 1$ state.

According to Figure 3, the electronic configuration of the $S = 2$ state may be described as $d_\pi{}^2 d_{xy}{}^1 d_{z^2}{}^1 d_{x^2-y^2}{}^1 d_{\pi'}{}^1$, with the following orbital energy ordering for the α-spin orbitals: $d_{xy} < d_\pi < d_{z^2} < d_{x^2-y^2} < d_{\pi'}$. The fact that the $d_\pi$ and $d_{xy}$ orbitals are low in energy is readily understandable in view of the discussion above (i.e., from elementary ligand field theory). The fact that the $d_{x^2-y^2}$ and $d_{\pi'}$ orbitals are relatively high in energy is also readily understandable in view of the antibonding interactions they involve. However, the relatively low energy of the $d_{z^2}$-based orbital is noteworthy. It indicates that the NN ligand, unlike simple nitrenes (i.e., alkylimido ligands), is a rather weak $\sigma$ donor. As mentioned above, no simple nitrene (or alkylimido) complexes of hemes have ever been reported, almost certainly because they are too reactive to be conveniently isolated and characterized.[11,14] Simple nitrenes (or alkylimido ligands) would strongly destabilize both $d_\pi$ orbitals and the $d_{z^2}$ orbital, leaving too few energetically accessible orbitals for the heme d electrons. Clearly, a very different scenario is involved for Fe(P)(NN).

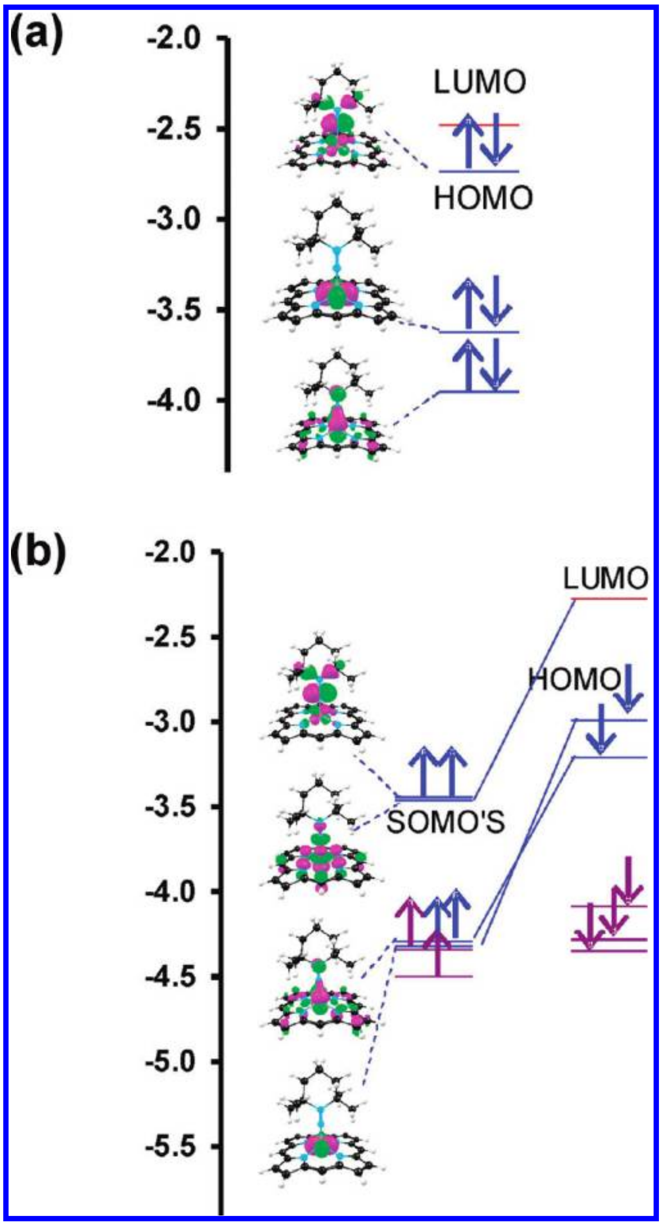

**Figure 2.** OLYP/TZP MO energy level (eV) diagrams for the lowest (a) $S = 0$ and (b) $S = 1$ states of Fe(P)(NN). MOs with substantial metal d character are indicated in blue, whereas those concentrated largely on the porphyrin are indicated in maroon.

Hydrazido ligands or aminonitrenes are electronically very similar to diazoalkanes,[32] which are relatively stable, neutral molecules with little nitrogen-based basicity to speak of. (It may be recalled that diazomethane preferentially protonates on the carbon.) Understandably, the NN ligand does not result in a serious destabilization of the $d_{z^2}$ orbital. Thus, despite the singly $\pi$-accepting nature of the NN ligand (which may be contrasted with the doubly $\pi$-accepting nature of CO and isocyanides), the overall d-orbital splitting pattern is not very different from that of a typical high-spin ferrous complex, which explains the $S = 2$ ground state.

Figure 4 depicts the OLYP spin density plots for the $S = 1$ and $S = 2$ states of Fe(Por)(NN). Compared to the axially symmetric spin densities of typical five-coordinate (deoxy) hemes (with $d_{xy}{}^2 d_\pi{}^1 d_{\pi'}{}^1 d_{z^2}{}^1 d_{x^2-y^2}{}^1$ electronic configurations),[33] the spin density of Fe(Por)(NN) is strongly anisotropic with respect to the Fe−NN axis.

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(32) For examples of Fe−diazoalkane interactions, see: (a) Bart, S. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 7212–7213. (b) Russell, S. K.; Lobkovsky, E; Chirik, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 36–37.

(33) The Fe−$N_{axial}$ bonding may be described as a $\sigma$ bond mediated by the $d_{z^2}$ orbital, a $\pi$ bond mediated by the $d_\pi$ orbital, and half a $\pi$ antibonding interaction due to the $d_{\pi'}$ electron, which together translate to a bond order of 1.5.

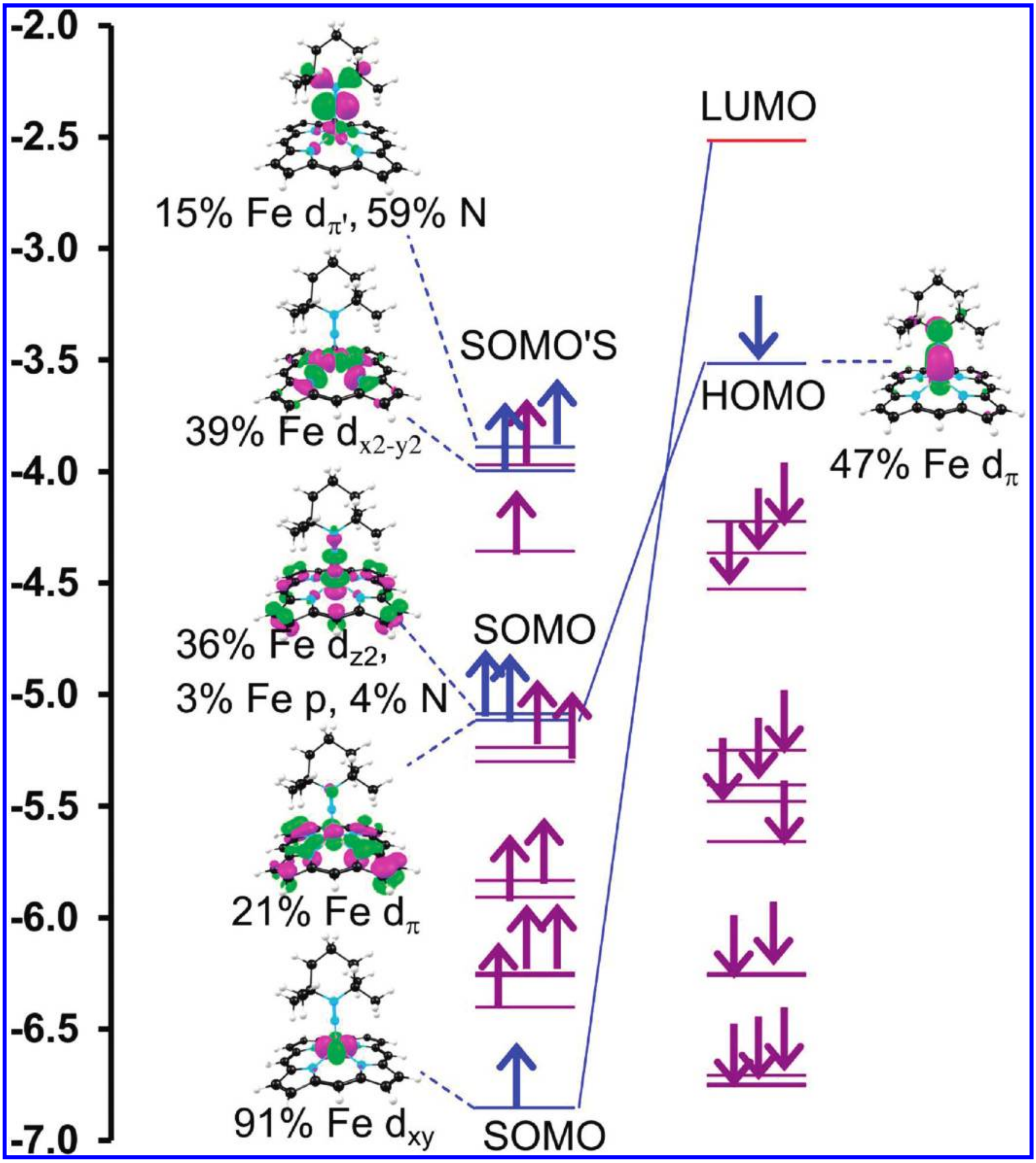

**Figure 3.** OLYP/TZP MO energy level (eV) diagram for the $S = 2$ state of Fe(P)(NN). MOs with substantial metal d character are indicated in blue, whereas those concentrated on the supporting porphyrin are indicated in maroon.

The anisotropy clearly results from unequal occupancy of the $d_\pi$ and $d_{\pi'}$ orbitals. The diazo unit carries only a small amount of excess spin density, which is significantly smaller than what is found on the oxygen atoms of $Fe^{IV}O$ intermediates[34] but not unusual compared with other $d_\pi^1$ metal-imido species, such as a $\beta$-diketiminatonickel(III) imido complex.[4]

**D. Explaining the Stability of Fe(Por)(NN) Species.** The MO picture presented above goes a long way toward explaining the stability of Fe(Por)(NN) complexes, relative to ordinary iron-porphyrin−nitrene intermediates. The fact that the NN ligand is a relatively stable diazo compound, as opposed to a simple nitrene, implies that

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[34] See, e.g.: Ghosh, A.; Tangen, E.; Ryeng, H.; Taylor, P. R. *Eur. J. Inorg. Chem.* **2004**, *23*, 4555–4560.

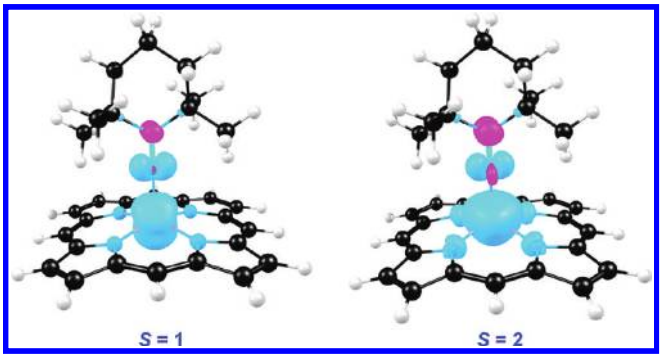

**Figure 4.** Spin density plots for the $S = 1$ and $S = 2$ states of Fe(P)(NN). Majority and minority spin densities are indicated in cyan and magenta, respectively.

Fe(Por)(NN) species should not be nearly as electrophilic as Fe(Por)(NR) (R = alkyl or aryl) intermediates or, for that matter, the compound I and II intermediates of heme proteins. This could be verified by means of explicit calculations of hydrogen atom affinities of Fe(P)(NN) and Fe(P)(NMe). Consider the following two reactions and the corresponding $\Delta E$'s, where the axial nitrogen atom closest to the iron abstracts a hydrogen atom from toluene, yielding high-spin Fe(III) porphyrins and a benzyl radical:

$$\mathrm{Fe(P)(NN)} + \mathrm{toluene} \rightarrow \mathrm{Fe(P)(HNN)}\ (S = 5/2) + \mathrm{benzyl\ radical},\ \Delta E = 1.86\ \mathrm{eV}$$

$$\mathrm{Fe(P)(NMe)} + \mathrm{toluene} \rightarrow \mathrm{Fe(P)(HNMe)}\ (S = 5/2) + \mathrm{benzylradical},\ \Delta E = -0.30\ \mathrm{eV}$$

The dramatic difference in the $\Delta E$'s provides a vivid illustration of the difference in reactivity of the two iron-porphyrin reactants. Thus, whereas the simple nitrene complex Fe(P)(NMe), which may also be viewed as an $\mathrm{Fe^{IV}}$-imido species, exhibits a clear propensity to abstract hydrogen atoms, Fe(P)(NN) does not; the high positive $\Delta E$ for the latter complex provides a numerical measure of its lack of reactivity, as well as an explanation for the experimentally observed stability of Fe(Por)(NN) complexes.

## Conclusion

DFT calculations have provided key insights into both the stability and the observed $S = 2$ ground state of an iron(II) porphyrin aminonitrene complex. The electronic configuration of this complex may be described as $d_\pi^{\,2} d_{xy}^{\,1} d_{z^2}^{\,1} d_{x^2-y^2}^{\,1} d_{\pi'}^{\,1}$, where the double occupancy of the $d_\pi$ orbital may be attributed to $\pi$-backbonding interaction with the N−N $\pi^*$ orbital. The weak $\sigma$-donor ability of the aminonitrene ligand results in a relatively low-energy $d_{z^2}$ orbital and an overall d orbital splitting pattern that engenders a high-spin ground state.

In an odd way, our findings on Fe(P)(NN), a rare non-low-coordinate iron-nitrene, strengthen our faith in the critical connection between low-coordinate architectures and the stability of middle and late transition metal imido complexes, a point we have emphasized throughout our theoretical work in this area.[4,6,8] The stability of Fe(P)(NN) thus should not be viewed as a counterexample to the general importance of low-coordinate architectures. Instead, Fe(P)(NN) is not a normal iron-nitrene or $\mathrm{Fe^{IV}}$-imido complex at all; it is an $\mathrm{Fe^{II}}$-diazo complex that is only very superficially related to other, relatively stable middle and late transition metal-imido complexes.

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**Supporting Information Available:** Optimized Cartesian coordinates for selected systems. This information is available free of charge via the Internet at http://pubs.acs.org.